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A review on nanostructured organic-inorganic hybrid coatings

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ABSTRACT

A thorough understanding of the corrosion thermodynamics and kinetics is first presented. Furthermore, the protective mechanisms of barrier, sacrificial, and inhibitive coatings are outlined. Sol –gel coatings and SNAP coatings are the focus of investigation in this review. In this article, recent developments in the processing stages and functional properties of the finally produced sol-gel-based hybrid coatings will be overviewed. Finally, some of the new and novel advancements in this area developed by different research groups will be discussed.

Keywords: Coatings, SNAP

Abbreviations: SNAP: Self Assembled Nanophase Particle

1. INTRODUCTION TO CORROSION

Corrosion can be defined as the gradual destruction of any reactive metal (Iron, copper etc) and their alloys by an electrochemical reaction resulting in their surface being oxidised. These metals are widely used in a plethora of different applications ranging from building materials to building aircrafts due to their excellent mechanical properties. These materials however are easily susceptible to deterioration by corrosion which is not only responsible for economic losses and technological delays but for structural failures which has a very detrimental impact on human beings and our surroundings. (Fragata, F, Salai, RP, Amorin, C, Almeida, (2006))

One of the most common types of corrosion is the formation of rust (Ferrous Oxide), which is generally formed due to the oxidation of steel surfaces. A metal oxide layer sometimes act as a protective layer for the underlying base metal and thus prevent it

from getting corroded but rust is not at all a preventive coating in any sense of the word. It generally promotes corrosion by attracting moisture/water and thereby acting as a catalyst for additional corrosion. There are numerous other promoters for the corrosion of ferrous metal such as dissolved salt, ammonia, dissolved solids etc. A second metal with a higher oxidation potential than the metal (iron) can also cause corrosion.

Corrosion can be of a localized type in which it generally forms pits or cracks or it can happen over a wide area with the corrosion being more or less uniform. Being diffusion controlled process; corrosion takes place on exposed surfaces. Therefore efforts to reduce the activity of the outer exposed surface, by passivation and chromate conversion, can significantly enhance a material's corrosion resistive properties.

Corrosion (direct and indirect) and its prevention costs are quite high. In fact it is calculated that it translates to a significant chunk of the net annual product in many countries. The total cost of corrosion in the US alone stands at an astounding $1 trillion dollars annually which is around 6.1% of the national gross domestic product. (Progress in Organic Coatings, 2006) As per estimations, the indirect cost of corrosion is at least equal to its direct cost.

Throughout the past few decades, there has been a significant increase in the use of organic as well as inorganic anticorrosive coatings for protecting metals. There has been significant progress in the fight against corrosion in various sectors of coating technology. For example, new corrosion resistant alloys have been developed which allows the operation of some critical processing equipment over a wide range of conditions. (P. A. Sørensen, S. Kiil, K. Dam-Johansen 2009) The oil and pipeline industry has also developed a cathodic protection method with advanced monitoring systems that allows safe operation under very difficult conditions. However, despite vast improvements in the different coating technologies, protection of metals in the long run under aggressive environments is still very challenging. The coating-substrate system is very complex and is a major reason why the number of high performance coatings (Anti-corrosive) is less. Apart from the primary ingredients of basic coating technologies which generally constitutes of solvents, binders, extenders, various additives and pigments, the durability and performance of anticorrosive coatings is dependent on various other parameters such as the substrate type used, its pre-treatment, curing, adhesion dynamics between the coating and substrate, thickness of the coating and various other external environmental parameters. Some of the desired characteristics of an anti-corrosive coating are intrinsic durability, toughness, adhesion to the substrate, flexibility and have no significant changes to its conformal identity in presence of external stress or weathering.

Corrosion occurs on the outermost exposed surface and it is an electrochemical phenomenon. If a metal "M" is exposed to oxidizing species, the following reaction occurs (Cathodic/ Anodic reaction)

- Anodic Reaction:

$$M \longleftrightarrow M_n^+ + ne^-$$

- Cathodic Reaction:

$$(n/4)O_2 + (n/2)H_2O + ne^- \longleftrightarrow nOH^-$$

- At Equilibrium:

$$I_a = |I_c| \quad \text{and} \quad I_a + I_c = 0$$

*I_a = anodic current; I_c = cathodic current

There is an electrical potential difference generated between the cathode and anode, which results in the formation of an electrical circuit, which catalyses the corrosion process. The completed electric circuit means there is a flow of electrons from a higher potential to the lower one (anode to cathode). If an insulator of some form is introduced between the cathode and the anode which would prevent the circuit from being completed, it would prevent the flow of corrosion current and thereby prevent corrosion. As discussed before, a passivating layer would prevent the substrate's exposure to water and oxygen and prevent corrosion. The other method to prevent rust formation is by Cathodic prevention in which the metal is brought in contact with a more active second metal.

2. CORROSION THERMODYNAMICS

If the chemical make-up of a particular environment is known, thermodynamics comes in hand (example Pourbaix or E-pH diagrams) to help find out the theoretical activity of a particular metal or alloy in a corrosion environment. But pragmatically speaking, the environment generally varies with different times and environments. The local environment about the metal surface is the environment that actually affects the metal. The reactivity of this micro-environment actually determines the corrosion damage.

(http://corrosion-doctors.org/Corrosion-Thermodynamics/Corrosion-Thermodynamics.htm) Thus, local effects like galvanic effect, pH cells, flow etc. should always be considered for its lifetime prediction.

In case of electrochemical and electrical processes, electrical work can be defined as the product of charges moved (Q) multiplied by the potential (E) in which the charges moved. If this work is carried out in an electrochemical cell where the potential difference between the two half-cells is E, and charge here is 1 mole of reaction within which a total of n moles of electrons are transferred, then -w (electrical work) of the cell would be nE. In this case, in order to obtain coulombs from moles of electrons, Faraday constant (F) would be required. When an electrochemical cell is at equilibrium, there is no flow of current and the change in energy that occurs in a reaction is expressed by the following equation:

$$W = \Delta G = -n F E$$

Under standard conditions, the standard potential difference (E^0) across the cell is directly proportional to the standard free energy (ΔG^0) of the cell reaction.

$$\Delta G^0 = -n F E^0$$

In case of elements or solid/liquid compounds, the standard conditions are the element itself or the pure compound. In case of gases, the standard condition is 100kPa pressure. For solutes, it is the ideal 1 molar (mol / L) concentration.

Cell potential is derived from combining the electrode potentials algebraically. In case of a galvanic cell, cell voltage is positive if the difference between the cathode and anode potential is taken, as in equation.

$$E_{cell} = E_{cathode} - E_{anode}$$

The change in free energy in case of either a spontaneous cell reaction or galvanic cell, negative but the cell voltage would have a positive value. Whereas in case of an electrolytic cell, an external potential needs to be applied for the continuation of the electrolysis reaction, the opposite is true.

Walther Nernst, the German chemist after whom the Nernst equation was named, established relations between the potential of a cell or the energy to varying concentrations of participating ions. Linking the free energy changes to the reaction coefficient, the following equation is derived which gives us the potential of the electrode.

$$E_{red} = E_0 + \frac{RT}{nF}\ln(X_{red} / X_{ox})$$

Where;

E_{red} = Half-cell reduction potential

X = Chemical activity of the relevant specie (X_{red} is the reductant and X_{ox} is the oxidant)

R = Universal gas constant (8.314 $JK^{-} mol^{-}$)

F = Faraday constant

E_0 = Standard potential of the cell

n = Number of electrons exchanged in the reactio

Some variable parameters such as the corrosion current and the rate of the electrochemical reaction are not considered in corrosion thermodynamic studies. Therefore, a study on corrosion kinetics helps us in considering the local environment about the metal surface which is the environment that actually affects the metal.

3. CORROSION KINETICS

The kinetics of corrosion reactions were introduced to give an insight to how fast corrosion reactions can occur. Consider the following reactions:

At anode: $Me \rightarrow Me^{n+} + ne^-$

At cathode: $Me^{n+} + ne^- \rightarrow Me$

At equilibrium:

$I_a + I_c = 0$ or $|I_a| = |I_c|$ where I_a = Cathodic current and I_c = Anodic Current

In case of non-equilibrium :
$|I_a| > |I_c|$ (The metal in this case is corroding)
$|I_a| < |I_c|$ (The metal in this case is being plated from the solution)

The Nernst equation in the above case is not obeyed and hence the actual potential is not same as the equilibrium potential: $E - E_0 = \eta$ which is the over potential or polarisation.

Butler-Volmer Equation is an important fundamental relationship in the field of electrochemical kinetics. It shows how an electrode's current is dependent on the potential of the electrode, when both the anodic and cathodic reactions take place on the same electrode. (http://www.doitpoms.ac.uk/tlplib/aqueous_corrosion/index.php) The following is a derivation for the reaction:

Every electrochemical reaction obeys the Arrhenius equation:

$$k = A \exp\left(-\frac{Q}{RT}\right)$$

In a similar way, the cathodic and anodic currents can be defined as:

Anodic current: $i_a = i_0 \exp\left(\frac{\alpha_a nF}{RT}\eta\right)$

Cathodic current: $i_c = \exp\left(\frac{\alpha_c nF}{RT}\eta\right)$

Where; i_0 is the exchange current density

The total current in the system is therefore the sum of the anodic and the cathodic currents:

$$i = i_0 \left\{\exp\left(\frac{\alpha_a nF}{RT}\eta\right) - \exp\left(-\frac{\alpha_c nF}{RT}\eta\right)\right\}$$ which is a simplified form of

$$I = A\, i_0 \left\{\exp\left(\frac{\alpha_a nF}{RT}(E - E_0)\right) - \exp\left(-\frac{\alpha_c nF}{RT}(E - E_0)\right)\right\}$$

Where i denotes the exchange current density, A is the area, α is the transfer coefficient and I is the total current.

The transfer coefficient value lies between 0 and 1 and generally found out to be ~1/2. The above form of Butler-Volmer equation holds when the electrical charge transfers at the electrode controls the electrode reaction (and not mass transfer from the electrode surface to the electrolyte and vice versa). Even then, Butler-Volmer equation is widely used by electrochemists.

In case of mass transfer controlled process, in the limiting current region, current density value is:

$$i_{LIMITING} = \frac{n F D}{\delta} C^*$$

This equation simplifies to the above mentioned conventional form when the concentration of electro active species in bulk is equal to that on the surface.

where: D= diffusion coefficient
δ = Diffusion layer thickness
C^* = electro active species concentration
C(0,t)= Time dependent concentration at zero distance from surface

There are however 2 cases in which the use of Butler-Volmer equation is limited:

- Polarization resistance (The low over potential region i.e. when $E \sim E_{eq}$) , the Butler-Volmer equation is modified to: $i = i_0 \frac{nF}{RT}(E - E_{eq})$
- The higher over potential region in which the Butler-Volmer equation modifies to form the Tafel equation:

$$E - E_{eq} = a - b \log (i) \text{ in case of a cathodic reaction when } E << E_{eq}$$

$$E - E_{eq} = a + b \log (i) \text{ in case of an anodic reaction when } E >> E_{eq}$$

Where a & b are the Tafel equation constants which have different theoretical values in case of anodic and cathodic stages.

The kinetics of the electrochemical reaction clearly denotes that the reaction rates of the anodic and cathodic processes of a system depend on the potential difference applied at the electrode. There are various other environmental parameters which also influence the rate of corrosion. For example, the corrosion rates generally increase with an increase in temperature. In case of normal marine immersion, for materials such as steel, the effect of an increase of temperature on corrosion rate is minimal due to the fact that these materials are directly affected by the oxygen content. With an increase in temperature, the water-solubility of oxygen would decrease and these effects tend to counteract each other. But for other alloys that are dependent on a passive film to help prevent corrosion, the effects of temperature are more pronounced. At higher temperatures, the oxygen solubility required for repair of the passivating oxide films is reduced and therefore the corrosive reactions that cause film break down are enhanced with an increase in temperature. Furthermore, the solubility of these corrosive species in dissolved oxygen, chlorides, hydroxides and carbon dioxide is dependent on the medium's actual pressure and temperature. Thus, a synergy of the corrosion kinetics, thermodynamics and local environmental conditions needs to considered for determining the most effective way of corrosion control

4. PROTECTIVE COATING TECHNOLOGIES

There are three basic protective mechanisms to inhibit corrosion (Zeno, W.; Wicks, J. F. N. J.; Pappas, S. P.; Wicks2007);

- Barrier Protection: The substrate is protected by a barrier which prevents the flow of aggressive species to it.
- Substrate Surface Passivation (Inhibitive effect): Developing a chemically inert layer by chemical conversion or by adding pigments which inhibit corrosion.
- Sacrificial Protection (Galvanic effect): The substrate is connected electrically to a more electrochemically active metal with both being in direct electrical contact.

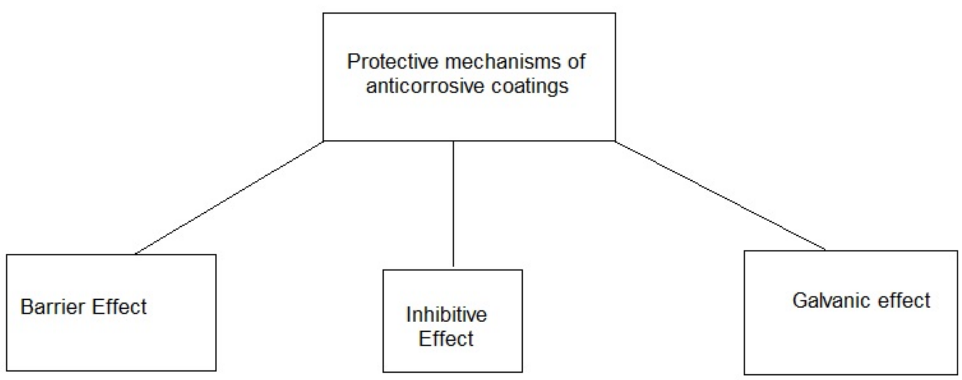

Figure 1
Different mechanisms by which anticorrosive coatings protect

4.1 Coatings based on barrier effect

The barrier coating can be used as all of the three types namely primer, topcoat or the intermediate layer. The mechanism by which these barrier coatings work is by ionic impermeability. (Fragata, F, Salai, RP, Amorin, C, Almeida2006) The electrical resistance on the surface is high due to the presence of moisture which causes the conductivity of the solution being very low at the substrate level which minimises current flow between the two electrodes. In general, polymer based coatings are applied which act as an effective barrier for corrosion. Fillers or pigments are generally introduced in these polymeric coatings which increases the length of the diffusion paths for the aggressive corrosion species. Micaceous iron oxide, halloysites, aluminium flakes, titanium dioxide, glass flakes are the generally used fillers. The volume concentration of the pigment is preferably kept low as this helps in the formation of a dense coating. The orientation of these pigments is parallel to the surface as it helps in creating a turquoise effect. The thickness of the barrier coating also determines the degree of corrosion protection. It has been found out that multiple successive thin layered coatings have better barrier properties than a single later coating of the same thickness.

4.2 Surface Passivation

An inhibitive coating would ideally have good barrier properties to water and oxygen and also be able to release inhibitor on demand. The inhibitive effect of the coating is however largely dependent on its barrier properties. Lead and chromium are the most

common compounds that are used as corrosion inhibitors for formulating anticorrosive primers for metallic substrate. Also, primers containing compounds such as metallic phosphate, silicate and molybdate are widely used. These pigments form a passivating oxide layer which impedes the flow of aggressive corrosive species. However, these chromate and lead based compounds are toxic and a suitable alternative must be found out. Organo-functional silanes have recently emerged as one of the alternatives for chromate treatment of metals due to it being environmental friendly. This technology is however limited as substrate must bear hydroxyl groups on the surface for the coating to take place.

4.3. Sacrificial Coatings

Sacrificial coatings based on galvanic corrosion's principle. This is achieved by having an electrochemically active metal (which is more active than the substrate) in direct electrical contact with the substrate. These sacrificial coatings are applied as primers because there is a need for direct electrical contact between the two metals. The density of pigmentation for sacrificial coatings is very high in order to achieve the metallic contact necessary for the flow of galvanic current. The use of sacrificial anodes like zinc to protect steel from corroding is a common industrial practice. The zinc layer which is deposited on the galvanized steel degrades in a corrosive environment which in turn protects the underlying substrate. This same approach has been used to develop a variety of zinc rich coatings which protect the metal substrates.

5 ANTICORROSIVE COATINGS

Anticorrosive coating systems generally have various layers with each layer having its own properties and use. The different coats maybe of metallic, organic or inorganic type. These individual components of the coating system are tailored to specific requirements needed. The various layers of the coating system are primer, topcoat and intermediate coats. The primer is primarily responsible for protecting the substrate and it also ensures adhesion of the other coatings to the substrate. The intermediate coats are generally responsible for increasing the thickness of the coating and thereby prevent the corrosive species from reaching the substrate surface. It should also have enough adhesion to bind the primer to the topcoat. The topcoat is the one that is exposed to the harsh environment and it should ideally have excellent resistance towards weathering and ultraviolet radiations.

Predicting a coating's performance and durability is very difficult because there are various other external and internal factors that influence its final outcome. Any final conclusion on a coating's anticorrosive performance on a specific substrate must be judged after its exposure to natural conditions in lieu with accelerated laboratory tests. There are various other in-homogeneities such as the presence of cracks, air-bubbles, voids, impurities and contaminants, non-bonded and trapped solvents which influence the transportation of corrosive species within the coating to the substrate-primer juncture. The process of coating the substrate must be carried out very carefully as any physical defect in the coating would severely lessen its lifetime. Inability of a coating to shrink can also cause an internal stress which also causes a severe reduction in the durability of the coating because it results in a reduction in adhesion or a cohesive failure.

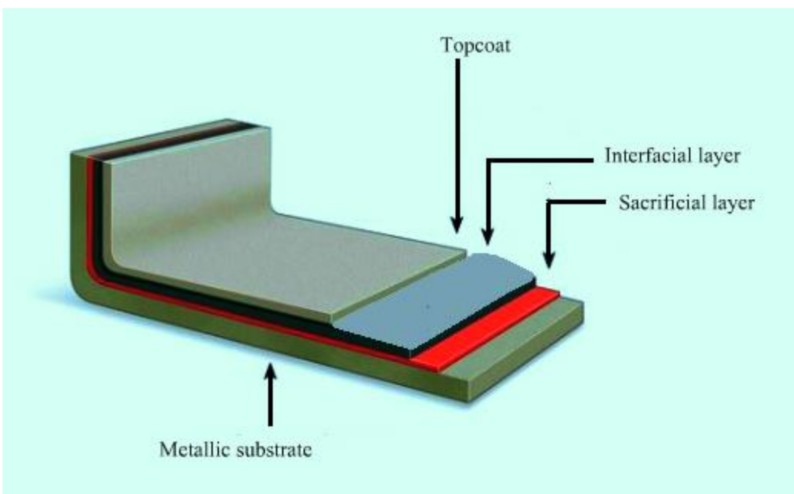

Figure 2
A systematic diagram of the different constituents of a multi-layered anticorrosive coating

Among all the coating types, multi-layered organic coatings are usually the most preferred barrier coating for metallic structures. Organic coatings are generally preferred due to its high cost effectiveness and have been very promising for preventing corrosion. This organic coating acts as a layer which prevents the diffusion of aggressive species. The interfacial adhesion between the metal surface and the coating and also the subsequent layers in case of a multi-layered coating is to be considered. This is due to the fact that delamination from the surface of the metal or the underlying layers is one of the main causes for coating failure. Several different types of polymer coating e.g. epoxy ester and alkyd systems, vinyl, styrene and polyurethane based coatings have been developed which could be used for corrosion protection. A multi-layered system of these organic coatings (as depicted in figure 2) is

considered to be most effective for corrosion protection. This multi-layered hybrid coating is composed of a primer layer that basically acts as corrosion preventing layer whereas the topcoat acts as the main barrier against the diffusion of aggressive corrosive species, oxygen and water.

Inorganic-organic hybrids are a very promising alternative due to its unusual features. The possibility to tailor the property of the final product by changing the compositions of inorganic and organic content has emerged in the last few decades. Some properties of these new developed materials are much improved than the cumulative properties of the constituent materials. Silicon based hybrids have started to generate interest and been used in the field of corrosion technology because:

- It improves the temperature and chemical resistance of different composites that can be used for coatings.
- It also increases inertness and is non-toxic
- Improves the mechanical strength, temperature stability and thermal shock resistance.
- Has better stability and wear resistance.

In the protective coatings industry various hybrid technologies are used such as sol-gel, epoxy (aliphatic) modified polysiloxane coatings, acrylic modified polysiloxanes, acrylosilane polymer etc. Sol-gel coatings are the one primarily in the context of this review.

5.1 Introduction to sol gel coatings

Sol-gel derived coatings are widely used as a protective layer for stainless steel and other structures. The sol-gel process is used to produce silicon based polymeric interpenetrating network in an organic binder medium. The sol is a colloidal suspension which is prepared from silicon-based-precursors, like tetra ethoxy silanes. The ethoxy silane is hydrolysed in an alkaline or acidic medium, resulting in the formation of silicon based sol in the organic binder. Among the several advantages of using sol-gel based coatings of which the main ones are (J.D.Wright, N.A.J. Sommerdijk 2001)(C.J. Brinker, A.J. Hurd, P.R. Shunrk .1992)

- Sol-gel reactions are generally carried out around room temperature. Therefore the degradation of species trapped in it is minimized. For example in case of organic inhibitors.
- As precursors are usually used in liquid form, it is viable to cast coat them into various shapes of different complexities and thereby manufacture thin films without needing hard-core machinery or melting.
- The toxicological impact of these sol-gel coatings to the environment is very low and is hence considered as a green coating technology. The method is completely free of toxic waste products.

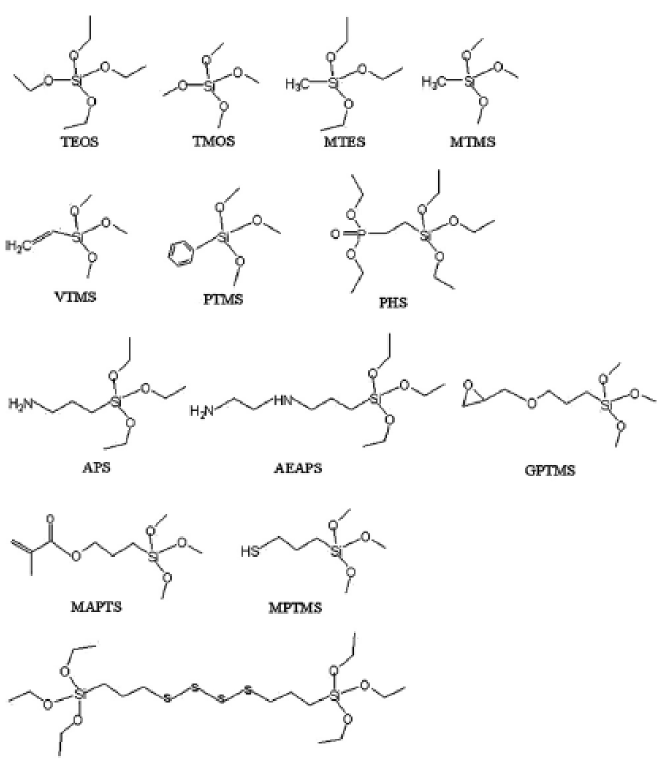

Figure 3
Alkoxysilane precursors for sol-gel coatings

5.1.1. Preparation of sol-gel coatings

In general, there are two major ways developed for the preparation of coatings using sol-gel method. One is based on the development of hybrid materials by means of chemical bonds (links) between the inorganic and organic phase through sol-gel reaction. Second method is based on the generation of nanoscaled "structures" of inorganic phase inside the organic component by sol-gel technique, which is generally referred to as SNAP process.

Metal oxide precursors have been one of the main starting species in development of hybrid coatings. The application of these precursors have resulted in inorganic coatings with good corrosion resistance and protection properties; however, in order to eliminate some of their drawbacks such as brittleness and high processing temperature, an organic component is required in their chemical structure. Some of the important organic alkoxysilane precursors (Figure 3) that have been used in developing sol-gel hybrid anticorrosive coatings especially for steel substrates are given in Figure 3

The formation of sol-gel takes place in 4 primary stages namely hydrolysis, condensation of the precursors to form long chains and particles, particle growth and agglomeration of the polymer structures to form networks which results in the formation of a gel. (DuhuaWang, Gordon. P. Bierwagen.2009) Once the hydrolysis reaction starts, the hydrolysis and condensation occurs parallel to one another. As evident from Figure.3, low molecular weight products such as water and alcohol are formed as by-products of hydrolysis and condensation.

The inter-crosslinking of the particles, stability of sol and the size of sol particles depend on factors such as pH, the water to silane ratio and various other variables. The sol is of low viscosity which becomes a three-dimensional network upon crosslinking and thus becoming a gel. The poly-condensation after the sol-gel process can occur either at the time of manufacture of the coating or after applying the coating on the substrate. Curing in some cases at elevated temperatures also causes poly-condensation. High scratch resistance, long durability and weathering are some properties as result of combining the silicon network inside the organic binder system. In order to meet specific characteristics, some ceramic nanoparticles can be incorporated in the sol-gel.

Sol-gel coating on metal surfaces are generally carried out by methods such as dip- and spin-coating (R.L. Parkhill, E.T. Knobbe, M.S. Donley 2001, A.L.K. Tan, A.M. Soutar, I.F. Annergren, Y.N. Liu 2005), (B. Veeraraghavan, B. Haran, D. Slavkov, S. Prabhu, B. Popov, B. Heimann 2003), (M. Sheffer, A. Groysman, D. Mandler2003) Emergence of new coating technologies such as electro-deposition and spray coating has huge potential in the near future. But irrespective of the method used for making sol-gel coatings, crack forming potential is quite high due to the presence of consistent voids or channels in the gel and therefore adequate protection is not provided. Also, in traditional sol-gel the maximum coating thickness is low. Some studies have shown than incorporating some nanoparticles into the sol can increase the coating thickness, without having any effect on the sintering temperature. (M. Atik, F.P. Luna, S.H. Messaddeq, M.A. Aegerter 1997) When we incorporate nanoparticles into the hybrid sol-gel, the cracking potential as well as the porosity is lowered and therefore the corrosion protection property is enhanced. Recent development have been carried out on inserting corrosion inhibitors, and preparation of Nano-reservoirs carrying corrosion inhibitors which act as self-healing materials with a controlled release profile. The method of forming functional silica nanoparticles in-situ and thereafter crosslinking it has been a recent discovery which shows the application of nanotechnology in coatings.

The combined use of these precursors has developed coatings with enhanced corrosion prevention properties, chemical flexibility and the possibility of developing defect-free smooth thin films. Jena et al. (Jena, K. K.; Rout, T. K.; Narayan, R.; Kothapalli, V. S.; Raju, 2012) has recently used ZnO nanoparticles modified with aminopropyltriethoxysilane to generate NH2 groups on the surface of the particles. Then, such particles have been mixed with NCOterminated PU to obtain a hybrid with superb anticorrosion and impact-resistant properties with strong film-metal adhesion.

Hammer et al. (Hammer, P.; Dos Santos, F. C.; Cerrutti, B. M.; Pulcinelli, S. H.; Santilli, C. V 2012) prepared hybrid coatings using acid catalyzed condensation of TEOS/MPTS (triethoxyortho-silicate/3-mercaptopropyltrimethoxysilane) mixture followed by radical polymerization of methyl methacrylate for steel substrates. They incorporated81 carbon nanotubes (CNTs) in order to reinforce and thus obtained hybrid coatings with brilliant anti-corrosive properties with resistance of up to 1 GΩ determined by impedance spectroscopy. They reported that incorporation of CNTs increased the stability of hybrid network possibly by formation of covalent bonds with siloxane group.

A lot of focus has also been on sol-gel-based anticorrosive coatings with corrosion-inhibiting characteristics. Mallakpour et al. (Mallakpour, S.; Dinari 2012) synthesized a sol-gel-based polyimide-TiO2 hybrid coating anticorrosive coating. The coating was prepared using a solution of titania precursor in polyamic acid, which was followed by removal of the solvent and imidazation. The elemental analysis confirmed the formation of Ti-O-Ti bond and microscopic images revealed the generation of TiO2 nanoparticles inside the polymer matrix. The benzimidazole pendant proposed a potential of this coating for corrosion prevention applications.

5.2 Hybrid coatings developed by the SNAP process

The self-assembled nanophase particle (SNAP) is based on the presence of hydrolysed silanes on the surface, is free of toxic chromium containing compounds and organic solvents. These SNAP coatings provide barrier type anticorrosive properties and they can be of a suitable replacement for chromium based surface treatment that is currently relevant. The freedom to design the coating starting from a molecular level is a very desirable property. Using the SNAP process, it is possible to make ultrahydrophobic coatings through the strategy of a hierarchical particulate additive. Particles of various sizes may be formed by growing the surface features in nanometer range. The composition as well as the geometrical integrity of the surface may be altered in order to have a control over wettability. Coatings based on SNAP in a matrix (polymeric) may be a possible way to make hydrophobic surfaces as it has a strong covalent bonding at the junction of the coating and the substrate. SNAP coatings depend on green chemistry in order to

generate Nano sized particles having an inorganic core and a surrounding layer of organic (Pathak, S. S.; Khanna2008). The SNAP nanoparticles formed are crosslinked using an organic crosslinking agent which results in a dense, particulate network which acts as an anti-corrosive coating. Several properties of these hybrid coatings are enhanced such as toughness, durability, barrier properties and resistance towards getting oxidised. SNAP coatings are based on nanosized silane macromolecules, which are preformed in solution and cross-linked on coating application. After the nanoparticles are formed in the solution, cross-linking agents are then added to chemically connect the nanoparticles, thereby forming the organic coating. SNAP is a versatile approach, and this approach for such interfacial bonding is through the application of sol-gel coating, which will provide inorganic functionality for bonding to the metal substrate and tailorable organic functionality for interaction with subsequent polymer layer (Figure 4) A SNAP coating relies on environmentally friendly wet chemistry to generate nanoscale particles with an inorganic core and an organic exterior. By preforming the SNAP "nanoparticles," the SNAP system does not rely on the pore forming hydrolysis and condensation reactions for curing. Organic cross-linking agents are then added to the solution to cross-link the particles, forming a dense, protective coating on the substrate.

Donley *et al* (M.S Donley, A.N Khramov 2009) had mentioned about the three different steps involved in the SNAP process. The first is the sol-gel reaction phase where the hydrolysis and simultaneous condensation reactions take place. In the second step, crosslinking takes place by the addition of the cross linker. Lastly, the solution is applied on the substrate and the film is cured.

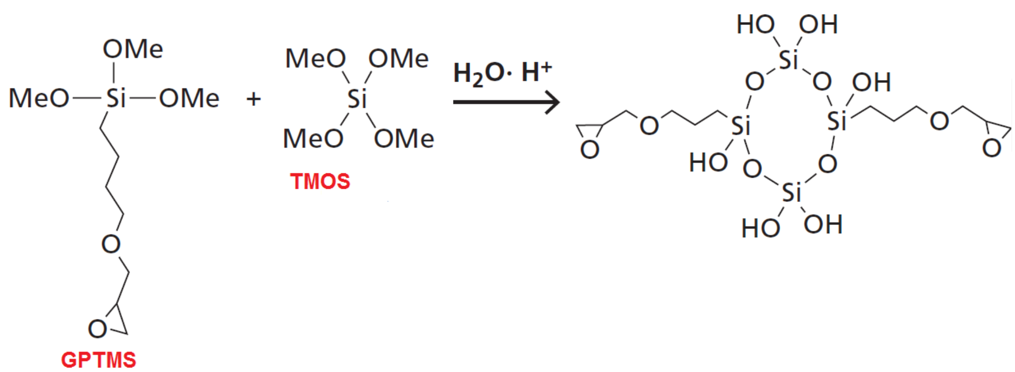

Figure 4
Mechanism of SNAP coating process

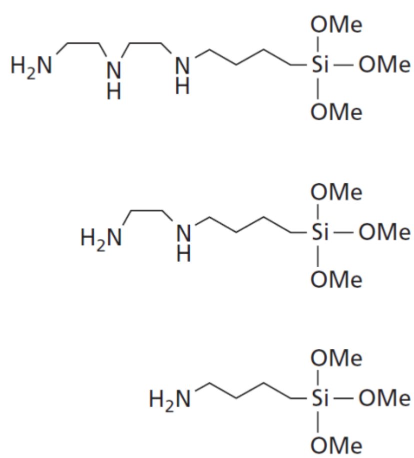

Figure 5
Different amino silane cross linkers

Voevodin et al. (Voevodin, N. N.; Kurdziel, J. W.; Mantz 2006) developed a modified SNAP formulation where they used TEOS along with GPTMS instead of using TMOS to produce SNAP coatings which were much less toxic. Additionally the methanol exposure in the second step was cut out. Zandi-zand et al. (Zandi-zand, R.; Ershad-langroudi, A.; Rahimi 2005) prepared a sol-gel solution of GPTMS and TMOS. A novel crosslinkerbisphenol A was used as the cross-linking agent in preparation of SNAP coating. Their results indicated a massive improvement in anticorrosion properties of hybrid coatings on aluminum substrates.

Kharmov et al. (Khramov, A. N.; Balbyshev, V. N.; Voevodin, N. N.; Donley, M. S. 2003) worked on the influence of cross-linkers with varying active amine groups (as shown in Figure 5. It was shown that aminosilanes can undergo hydrolysis and condensation as

well as cross-linking reactions, so they can be considered as dual-functional agents in SNAP coatings. Their data revealed that application of "3A" agent (Figure 6) with highest active amine content in sol-gel formulation, produced SNAP coating with superior properties compared with "2A," "1A".

6. CONCLUSION

There is certainly a better understanding of the local and semi-local structures developed in the novel hybrid structures now using the sol-gel route. There is a substantial increase in the adhesive and anti-corrosive properties by chemically manipulating the constituent organic and inorganic species. These hybrid species reflect a significant development of hybrid materials which resemble the original properties of its constituents, such as the toughness and flexibility shown in case of organic species along with the passivating nature of the inorganic phase. To have a greater amount of control over the material structure, self-assembling nano-building blocks is a very promising approach. The structure of the inorganic components which are mono-dispersed and well defined helps in characterizing the final developed materials. Due to the vast pool of these nano-building blocks and the corresponding links, they allow for a variety of organic-inorganic interfaces to be formed. Despite these significant advancements made in the field of sol-gel based coatings, there is still a lot to be desired in having anticorrosive coatings with a significant lifetime.

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